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Neutron-scattering study of chain-oxygen vibrations in $YBa_2Cu_3O_7$

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The *ab*-plane-polarized transverse chain-oxygen vibrations in $YBa_2Cu_3O_7$ were investigated by inelastic neutron scattering on an untwinned single crystal at different temperatures. From the rather high frequencies of these modes ($\nu \approx 5$ THz), the moderate phonon linewidth, and the absence of an appreciable frequency shift with temperature, we conclude that the chain-oxygen vibrations are not strongly anharmonic. Concurrently, diffraction data are incompatible with a wide double-well potential for the chain-oxygen atoms.

There are numerous suggestions (e.g., Refs. 1 and 2) that anharmonicity may be important to explain the high T_c's in the cuprate superconductors. If the ions are moving in a double-well potential, an order-of-magnitude enhancement of the electron-lattice coupling may be expected due to the very large scale of the atomic displacements. At the same time, the isotope effect may be partly suppressed, thus offering a possibility to reconcile the low values of the isotope exponent found in experiment with a phononic mechanism for superconductivity also in the cuprates.

The presence of anharmonic vibrations in $(La,Sr)_2CuO_4$ is well established. Those are the tilting motions of the Cu-O octahedra related to the tetragonal-to-orthorhombic phase transition. Here, we do not want to enter into the discussion if the tilting modes in $(La,Sr)_2CuO_4$ are really relevant for superconductivity, but instead deal with the question of whether there is evidence for strong anharmonicity in $YBa_2Cu_3O_{7-x}$ as well. As $YBa_2Cu_3O_{7-x}$ does not show a structural phase transition, there is no analog to the soft tilting mode in $(La,Sr)_2CuO_4$ as an obvious candidate for strongly anharmonic lattice vibrations. Structural data[3,4] as well as frozen-phonon calculations[5] suggest that the potential seen by the chain-oxygen atoms when vibrating in the (100) direction may be very anharmonic, favoring a "zigzag" distortion of the chains. From their calculations Cohen, Pickett, and Krakauer[5] concluded a wide double-well potential with a width of 0.5 Å between minima, which may be important for superconductivity because of the large weight of the chain-oxygen electronic states at the Fermi level. This stimulated us to perform an inelastic-neutron-scattering study of the transverse chain-oxygen vibrations which will be reported in the following.

The sample was a single crystal grown in a Y_2O_3 stabilized ZrO_2 crucible using the eutectic composition of the $BaCuO_2$-CuO side system as a flux.[6] Subsequently, the sample was annealed in flowing oxygen at 450 °C for 10 days. The oxygen content was estimated to be $O_{6.95}$. The superconducting transition temperature was found to be $T_c = 92$ K. In order to make the sample monodomain, the crystal was ground into a rectangular shape and loaded with a uniaxial pressure of 1 kbar at a temperature of 450 °C. Detwinning was monitored using a hotstage polarization microscope. The short duration of the treatment (~ 10 min) as well as the fact that the treatment was performed in flowing oxygen, ensured that the oxygen content of the crystal was not affected. From neutron-diffraction measurements we conclude that we achieved a volume ratio of the two domains of about 20. The final dimensions of the sample were $4 \times 6 \times 0.5$ mm^3.

The neutron measurements were performed on the 2-T triple-axis spectrometer located at a thermal beam tube of the ORPHEE reactor at Saclay. Horizontally and vertically focusing Cu(111) and pyrolithic graphite (002) crystals were used as monochromator and analyzer, respectively. The final energy was fixed at $E_F = 3.55$ THz, which allowed the use of a graphite filter in the scattered beam to suppress higher-order contamination. The temperature was varied between room temperature and 20 K.

Our search for phonon peaks associated with transverse chain-oxygen vibrations was guided by lattice-dynamical calculations based on fits to data taken on twinned samples.[7] The model predictions for frequencies and intensities were largely confirmed by our measurements on the untwinned sample, thus providing a reliable basis for the assignment of the observed neutron groups. In the following, we will concentrate on modes polarized in the basal plane. Modes polarized along *c* will be dealt with at the end of the paper. The displacement patterns of the zone-center and zone-boundary modes involving transverse chain-oxygen vibrations along the x direction are displayed in Fig. 1. We note that the chain-oxygen vibrations may mix with modes involving displacements of other atoms. From symmetry considerations as well as from calculations using various lattice-dynamical models we expect a nearly pure chain-oxygen mode for $\mathbf{q}=(0,0.5,0)$ and $\mathbf{q}=(0.5,0.5,0)$, whereas the situation is less clear-cut at the zone center. We will come back to this point at a later stage.

The largest experimental effort was devoted to study the zigzag mode at $\mathbf{q}=(0,0.5,0)$ to check the theoretical prediction made by Cohen, Pickett, and Krakauer.[5] Representative room-temperature data are shown in Fig. 2. According to our analysis the peak seen at $\nu=4.2$ THz arises from two branches having nearly the same frequency and involving Y and Cu(1) apical oxygen vibrations, respectively. The peak at $\nu=5.9$ THz corresponds to Cu(2) vibrations. The peak at $\nu=5.1$ THz, which is seen only in the scan at $\mathbf{Q}=[2,0.5,0]$, corresponds to transverse chain-oxygen vibrations polarized along [100]. This assignment is based not only on the striking difference between the intensities observed at $\mathbf{Q}=[2,0.5,0]$ and $\mathbf{Q}=[0.5,2,0]$, but also on the absence of these peaks in scans on $YBa_2Cu_3O_6$ (O_6), whereas the other peaks do have counterparts. The relevant branches found in O_6 and O_7 are shown in Fig. 3.

We note that a frequency of $\nu=5$ THz is by no means low and fits perfectly well to what we expected from our *harmonic* model. On cooling to $T=50$ K, the frequency increases slightly, i.e., $\Delta\nu/\nu \lesssim 2\%$, as is commonly found for weakly anharmonic solids, whereas double-well potentials are associated with soft-mode behavior. From the peak width at $T=300$ K we obtain, after correction for the instrumental resolution, $\Delta\nu/\nu \approx 7\%$, which might be indicative of mode-rate anharmonicity. Surprisingly, we did not observe a narrowing of the line on cooling, as is usually found in anharmonic solids.

The theoretical predictions of Cohen, Pickett, and Krakauer[5] were not the only reason to expect a strongly anharmonic potential for the chain-oxygen vibrations; as will be discussed below, structural data[3,4] revealed an unusually large Debye-Waller factor for the chain oxygens in the x direction. Therefore, although the zigzag chain-oxygen mode $\mathbf{q}=(0,0.5,0)$ was stable, unstable modes might be found in other parts of the Brillouin zone. To check this we investigated the branches starting from $\mathbf{q}=(0,0.5,0)$ in the $(0,\xi,0)$ direction to the zone center and in the $(\xi,0.5,0)$ direction to $\mathbf{q}=(0.5,0.5,0)$. When going along the $(\xi,0.5,0)$ direction it became increasingly difficult to separate the relevant peaks from other phonon groups, but there was no doubt that the frequency of the chain-oxygen vibrations does not decrease when going to $\mathbf{q}=(0.5,0.5,0)$. This is in agreement with the predictions of lattice-dynamical models and can be understood by the fact that the Coulomb forces between the chain-oxygen atoms in neighboring unit cells produce a restoring force for the mode at $\mathbf{q}=(0.5,0.5,0)$, but not at $\mathbf{q}=(0,0.5,0)$.

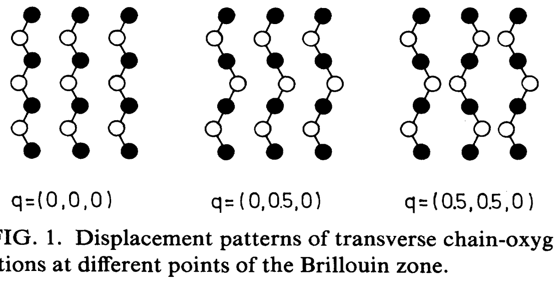

FIG. 1. Displacement patterns of transverse chain-oxygen vibrations at different points of the Brillouin zone.

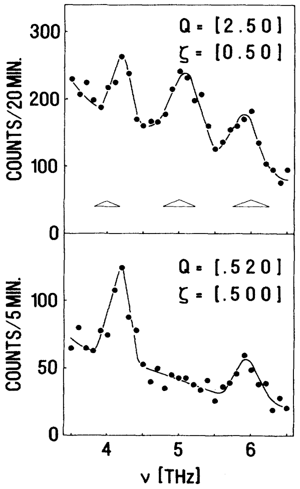

FIG. 2. Representative data taken on an untwinned crystal at room temperature. Lines are a guide to the eye only. Triangles denote the instrumental resolution.

As shown in Fig. 3, little dispersion was found also for the pertinent phonon branch in the $(0,\xi,0)$ direction. Therefore, it is tempting to conclude that the chain-oxygen vibrations are not soft at the zone center (Γ), too. However, model calculations showed that this conclusion might be premature: at Γ, there are three modes which may have an appreciable chain-oxygen character, the mode observed at $\nu=5$ THz being the highest of the three. We learned that models can give a very low or even imaginary frequency value for the lowest mode while reproducing the flat branch at $\nu=5$ THz fairly

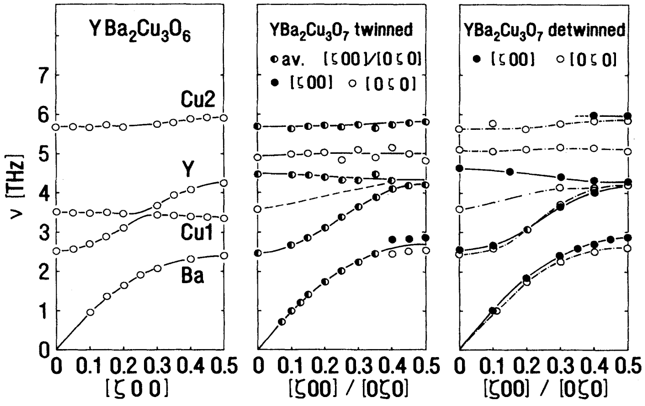

FIG. 3. Selected phonon branches are observed in O_6 (Ref. 7), in a large twinned sample of O_7 (Ref. 7), and in the untwinned O_7 sample of the present study. Lines are a guide to the eye.

well. Therefore, we checked the model predictions for all the branches below 5 THz and came to the following conclusion: The lowest zone center mode involving appreciable chain-oxygen elongations has a frequency of $\nu = 2.5$ THz. It shows neither a strong broadening nor an unusual temperature dependence. Furthermore, the related mode in O_6 has practically the same frequency. In conclusion, the phonon data do not show any evidence for a near instability involving chain-oxygen displacements.

An independent check, whether the chain-oxygen atoms are sitting in a double-well potential, can be made by highly precise diffraction measurements which allow us to determine average displacement amplitudes of the individual atoms. Such measurements were done on a twinned single crystal with composition $YBa_2Cu_3O_{6.98}$ at $T = 300$, 90, and 45 K using neutron diffraction. The full results of this study will be presented elsewhere.[4] Here, we want to concentrate on the mean-square displacements of the chain-oxygen (O_1) ions. Figure 4 shows the temperature-dependent anisotropic thermal parameters for O_1 as deduced from the diffraction data and as expected from the lattice dynamics in the framework of a harmonic model fitted to the phonon data. For comparison, the corresponding values for the apical oxygen (O_4) ions are given as well. As has been found by other groups,[3] $U_{11}(O_1)$ is unusually large. Figure 4 shows that the temperature dependence of $U_{11}(O_1)$ can be well understood by a harmonic model, but there is an additional component contributing to $U_{11}(O_1)$, which may be of static origin. We tried the hypothesis of static zigzag displacements, but found no better agreement with the diffraction intensities than for random displacements. The diffraction data do not rule out zigzag displacements, but in any case, the amplitude of such displacements has to be much smaller than predicted by Cohen, Pickett, and Krakauer,[5] i.e., only about 0.07 Å instead of 0.25 Å.

Static displacements may originate from disorder, such as nonstoichiometry, antisite defects, domain boundaries, etc. Disorder-induced static displacements may be the reason that the thermal parameters deduced from the diffraction data were found to be in general slightly larger than expected from the lattice dynamics. However, the difference is relatively large for $U_{11}(O_1)$ and we do not see why this parameter should be more sensitive to sample imperfections than the other ones. In addition, measurements made on several samples with different rare-earth ions do not show much scatter for $U_{11}(O_1)$,[4] suggesting that the large values of this parameter are an intrinsic property. This makes the hypothesis of static displacements somewhat unplausible, but on the other hand, we consider it very unlikely that $U_{11}(O_1)$ is entirely dynamic in nature: larger values of $U_{11}(O_1)$ than calculated from our harmonic model can be expected only if the potential is very anharmonic. This must not necessarily mean a double-well potential, but at least a potential with a wide flat bottom. However, the fact that neither the zone-center nor the zone-boundary chain-oxygen vibrations showed a significant temperature dependence of the frequencies, points against a flat-bottom potential. In any case, the observed values of $U_{11}(O_1)$ are an upper limit to dynamic displacements which are much lower than expected from the predictions of Cohen, Pickett, and Krakauer.[5]

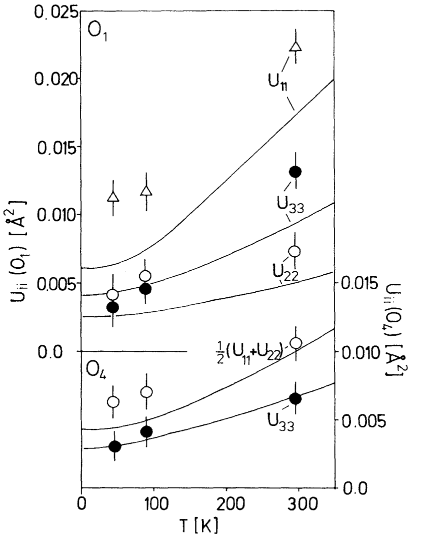

FIG. 4. (Top): Anisotropic thermal parameters for the chain-oxygen ions (O_1) as deduced from diffraction measurements on a twinned single crystal of O_7 (Ref. 4). Lines were calculated from a lattice-dynamical model assuming harmonic vibrations. (Bottom): The same as (top) for the apical oxygen ions (O_4).

So far, we focused on the transverse chain-oxygen vibrations polarized in the basal plane. We note that the corresponding vibrations polarized along *c* were found to be considerably higher in frequency, i.e., above $\nu = 8$ THz. This can be explained by the fact that the Coulomb repulsion between the apical and the chain-oxygen ions tends to destabilize the in-plane transverse chain-oxygen vibrations, but produces a large restoring force for displacements along *c*. As a consequence, the chain-oxygen potential will not show any tendency towards a double-well shape when viewed along *c*.

In conclusion, both the phonon and the diffraction data show that the transverse chain-oxygen vibrations are only moderately anharmonic. The results are incompatible with a wide double-well potential. In particular, the zigzag pattern investigated by frozen-phonon calculations[5] was found to be fully stable. Assuming that the potential is of the double-well type, we obtain $\Delta x = 0.07$ Å as an upper limit for the distance between the center and the minima, which is not more than the zero-point motion amplitude, and much smaller than predicted from band theory.[5] We cannot comment on why band theory failed in this case, but we know from calculations using empirical interatomic potentials[8] that it is difficult to avoid unstable chain-oxygen vibrations at the zone center. This indicates that already minor errors associated with the local density approximation might have produced an unstable zigzag mode.

A moderate anharmonicity is probably not important for superconductivity. It has been pointed out by Hui and Allen[9] that anharmonic single-well potentials will not enhance the electron-phonon coupling strength λ compared to a harmonic potential giving the same phonon frequencies. As the chain-oxygen vibrations are not anomalously soft, anharmonicity can only moderately, if at all, increase the coupling strength of the chain-oxygen ions.

In this paper we concentrated on transverse chain-oxygen modes as the most likely candidates for strongly anharmonic lattice vibrations. Before concluding that anharmonicity is unimportant for the high T_c of O_7 it would be necessary to study other phonon modes as well. Many further measurements have indeed been performed aiming at a full set of phonon dispersion curves. Although no special effort was undertaken to search for anharmonic effects, we note that none of the many phonon branches below $\nu = 10$ THz investigated showed evidence of strong anharmonicity. In particular, the often discussed apical oxygen motions along z are likewise not a good candidate for strongly anharmonic lattice vibrations: as can be seen from Fig. 4 (bottom), the mean-square displacements of the apical oxygen ions in the z direction are rather small and can be fully explained by a harmonic model.

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